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Effect of Microbial Activity on Cd Sorption/Desorption Processes in Soil Polluted with Various Cd Sources

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1. Introduction

Levels of heavy metals in soil are increased by the deposition of fly ash from coal combustion plants, disposal of municipal waste, use of fertilizers or other soil additives, and indirectly by industrial activities. Phytoremediation is a technology which uses plants and their associated rhizosphere microorganisms to remove pollutants from contaminated environmental media (soil, sediments, ground and surface waters) [12]. For plant uptake, soluble fractions of heavy metals must be present in the soil solution. Availability of metalic ions to the plant is controlled by mobilization of metal adsorbed to the solid phase of soil [3]. The activity of root– and soil– colonizing microorganisms can significantly influence the bioavailability of heavy metals for plant uptake by changing soil properties such as pH and the concentration of ligands in the soil solution [12].

The aim of this study was to determine the size of bioavailable fraction of cadmium mobilized from two soil samples and to estimate simultaneous sorption of the mobilized metal by constituents of the solid phase of soil. The two soils used in the experiments were zinc smelter – contaminated soil collected in Miasteczko Śląskie (MS) and soil fertilized with sewage sludge (SS).

2. Methods

A multi-chamber system consisting of one central chamber and 6 side chambers separated by membrane filters was used in the experiment [10]. A water extract from root-free soil (RF) [9] sterilized with filtration or the same extract enriched with glucose (RFG) – to simulate increased contents of nutrient in the rhizosphere [7], was introduced to the central chamber. The contaminated soil and soil constituents [clay, biomass isolated from a rye rhizospher: bacterium (*Arthrobacter*) and fungus (*Trichoderma*), humic acid and goethite] were introduced to the side chambers. The soil extract could circulate in the system but the membranes located between the central and side chambers prevented transfer of microorganisms. Changes in Cd concentration in the soil, the circulating soil extract, and in individual soil constituents during 48 hours of incubation at 14^{o}C were determined by the ASS method [6, 8]. Changes during the incubation in the cfu number of bacteria and fungi colonizing contaminated soil, as well as those used as soil constituents (*Arthrobacter* and *Trichoderma*) were estimated by the plate method [1, 11]. During the incubation period, changes in pH and in the concentration of microbial products able to chelate the metal in the soil extract circulating in the system were also determined [2, 4, 5]. The amount of Cd in the soil extract circulating in the system after incubation was recognized as bioavailable. Total concentration of Cd in the two contaminated soils was significantly different. The soil collected in the vicinity of the zinc smelter contained twice the amount of the heavy metal (10.7 μg g^1) as the soil amended with sewage sludge (5.2 μg g^1). In this situation, the changes in pools of Cd during the incubation period were expressed as changes in the percent of total metal concentration in a given soil.

3. Results

In both tested soils, Cd was mostly present as bound to Fe and Mn oxides, however, the content of this fraction in the MS soil was significantly higher. During incubation, an average of 60% of Cd was mobilized from this soil with the two soil extracts used. Much less Cd was mobilized from the SS soil, and though enrichment of the soil extract with glucose significantly enhanced its mobilization (from 35% to 50%). The metal removed from soil was in part resorbed by the soil constituents and some of it remained bioavailable (soluble) in the soil extract. The bioavailable pool of Cd mobilized from the MS soil was, on average, 5-times bigger than in the case of the SS soil. In both cases, enrichment of the RF extract with glucose resulted in an increase of the bioavailable pool of Cd. Cadmium mobilized from the MS soil with the RF extract was resorbed mostly by microbial biomass (60%), while that mobilized with RFG was resorbed predominantly by clay. On the other hand, cadmium mobilized from the SS soil with the RF extract was resorbed predominantly by inorganic soil contituents (70%), while that removed from the soil during incubation with RFG - by organic ones.

During incubation, there was proliferation of both microorganisms colonizing the contaminated soils (oligotrophic and copiotrophic bacteria and fungi) and those such as *Arthrobacter* and *Trichoderma*, present in the system as Cd resorbing soil constituents.

Enrichment of RF with glucose had a significant influence on the cfu number of the tested microorganisms, as well as on the pH of the soil extract circulating in the system and its content of siderophores and low molecular mass organic acids.

After incubation of both contaminated soils in the system with RFG circulating, the pH dropped by 3 (MS soil) or 1.5 units (SS soil). The concentration of catechol siderophores, citric acid and acetic acid in the soil extracts mobilizing Cd from the MS soil were significantly higher than in the extracts mobilizing Cd from the SS soil. Enrichment with glucose resulted in an increase of the concentration of acetic acid in extract mobilizing Cd from both soils, whereas the concentration of citric acid increased during the mobilization of Cd only from the MS soil, and hydroxamate siderophores – from the SS soil.

Statistical analysis of the obtained data indicated that pool of bioavailable Cd (the percentage of total cadmium remaining in soil extracts after resorption of mobilized Cd by soil constituents) was negatively correlated with pH in both tested soils (-0,70 for MS and -0.99 for the SS soil) and with the concentration of catechol siderophores in the mobilizing extract in the case of the SS soil. Also, negative correlations were found between pH and the concentration of citric (0.83) and acetic (-0.98) acids in soil extracts mobilizing Cd from the MS soil and between pH and the concentration of acetic acid (-0.76) in extracts mobilizng Cd from the SS soil.

Percentage of total cadmium resorbed (after its mobilization from both soils by soil constituents) was positively correlated with the concentration of hydroxamate siderophores in the soil extracts. High negative values of correlation coefficients were found between the percentage of bioavailable Cd in soil extracts and the cfu number of oligotrophs, copiotrophs, and fungi colonizing the MS soil (from –0.72 to –0.78) and *Trichoderma* introduced into the system as a soil constituent. In the system containing the SS soil, a similar correlation was found between the percentage of bioavailable Cd and the cfu number of oligotrophs (-0.93). High positive values of correlation coefficients were found between the percentage of Cd resorbed by soil constituents after its mobilizing from soil and the cfu number of oligotrophs and copiotrophs (0.93) colonizing the MS soil as well as the cfu of *Trichoderma*. In the system containing the SS soil, such correlation was found between the percentage of resorbed Cd and the cfu number of copiotrophs colonizing the soil and *Trichoderma* and *Arthrobacter* used as soil constituents.

4. Conclusions

1. The source of cadmium in contaminated soil had a significant influence on forms of this heavy metal (differing in their sorption affinity to soil constituents)

mobilized by soil extracts.

2. Enrichment of a soil extract with a nutrient substance (like in rhizosphere) enhanced proliferation of soil and rhizosphere microroganisms. The release of their metabolites into the soil extract as well as the increase of the biomass and significant changes in the soil's pH affected Cd sorption/desorption processes.

3. Catechol and hydroxamate siderophores synthesized by microorganisms and secreted into the soil extract affected Cd sorption/desorption processes in a different ways.

4. Organic acids (citric and acetic) produced by microorganisms were involved in acidification of soil extracts.

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